

Mechanism study of condensed drops jumping on super-hydrophobic surfaces

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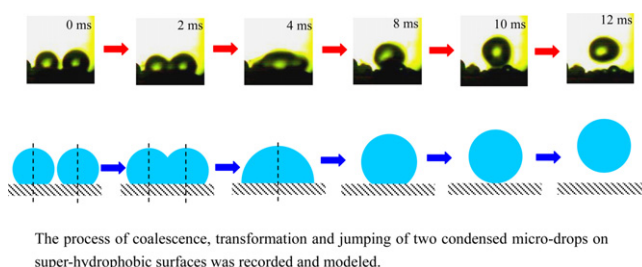
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HIGHLIGHTS

- ▶ Initial shape of a coalesced droplet is determined based on energy conservation.
- ▶ The driving force and resistance during drop transformation are analyzed.
- ▶ A dynamic equation describing shape conversion of a droplet is proposed and solved.
- ▶ Merged droplets jump because they are in unstable state on nanostructure surfaces.

GRAPHICAL ABSTRACT

The process of coalescence, transformation and jumping of two condensed micro-drops on super-hydrophobic surfaces was recorded and modeled.



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ABSTRACT

The out-of-plane jumping motion of coalesced condensed drops on super-hydrophobic surfaces can potentially enhance dropwise condensation greatly. But the jumping mechanism is not clear. In this paper, the initial shape of a coalesced droplet is determined based on the conservation of drop interface free energy (IFE) and viscous dissipation energy before and after two or more condensed droplets merge. The coalesced drop is in unstable state with a driving force to reduce its base radius toward equilibrium state. Then, the driving force and resistance on three-phase contact line (TPCL) are analyzed during the drop transformation. And the dynamic equation describing the shape conversion of the droplet is proposed and solved. The jumping height of a merged drop is determined according to the up moving speed of drop gravity center when the base radius of the droplet reduces to 0. The calculation results show that a coalesced droplet on flat surface can transform its shape limitedly. It cannot jump since its transformation stops before it comes to its equilibrium state. A wetted drop on rough surfaces is even more difficult to transform and jump because of the greater TPCL resistance. However, on a two-tier surface, a partially wetted drop impaling only the micro-scale roughness exhibits a shape transition to Cassie state and possible jumping upon coalescence if the micro and nanostructure parameters are suitable. Furthermore, after the coalescence of two or more Cassie state drops with their scale range from tens micrometer to millimeter on a textured surface, the merged composite drop can easily transform until its base radius becomes 0 and then jumps. A too small or too large merged drop will not jump because the obvious viscous dissipation energy or drop gravity respectively dominates the behavior of the drop. Meanwhile the coalescence-induced jumping of two drops will also not take place if their scales are significantly different. It can be concluded that the key factors resulting in condensed drops jumping are the merged drop in unstable state with enough surplus IFE and small TPCL resistance on nano or micro–nano two-tier surfaces.

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1. Introduction

Condensation is an important and widely accepted heat transfer type in lots of industries and engineering processes, such as petrochemical industry, power industry, air conditioning and

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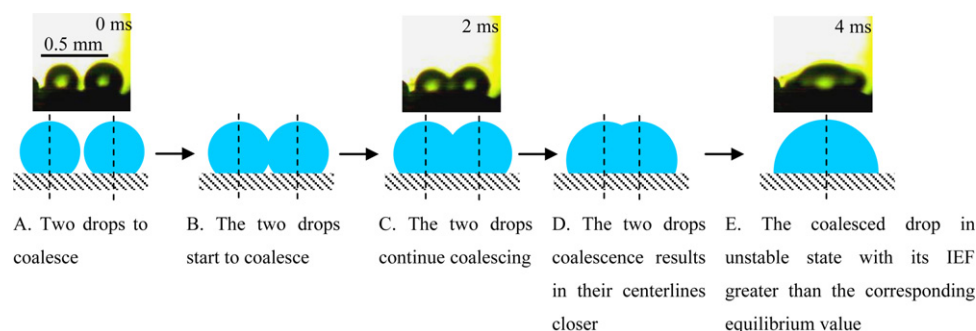


Fig. 1. Coalescing process of two droplets. *Upper photos:* side-view imaging of two condensed drops with diameters of 302 and 252 μm during merging; *lower:* modeled coalescence process.

refrigerating process. And the heat transfer coefficient of dropwise condensation is much higher than that of filmwise condensation. It is therefore undisputed that the size of the heat exchangers and/or the energy consumption rate can be greatly reduced if dropwise condensation can be realized in those industries and processes [1].

It is possible to realize highly efficient dropwise condensation on super-hydrophobic surfaces with nano or micro-nano hierarchical architecture [2–7]. Lau et al. [2] firstly reported that Cassie state condensed drops stably appeared on the super-hydrophobic surface with carbon nanotube forest. Then, Chen [3] and Dorrer [4] respectively observed the fast moving of condensed drops upon coalescence on the super-hydrophobic surfaces with micro-nano or nano textures. These rapidly mobilized drops can sweep off other growing drops so that the condensed drops on surfaces can be quickly removed and dropwise condensation is thus enhanced. Afterwards, Chen [5,6] discovered a more interesting phenomenon, the self-propelled out-of-plane jumping motion of the coalesced drops with the size above 10 μm on two-tier textured surfaces, and Wang [7] also got a similar result. More recently, it was reported that both partially wetted and suspended droplets on super-hydrophobic nanostructured surfaces were observed to undergo coalescence-induced jumping [8]. This jumping motion results in small condensed drops off surfaces early, so that new nuclei can form and grow, and the average drop size reduces greatly. If both nucleation number and droplet departure frequency can also increase, the dropwise condensation could be enhanced significantly.

Although the self-propelled jumping phenomenon was discovered three years ago, its detailed mechanism is still not very clear to date. The current explanation is limited to the excess surface free energy possessed by a coalesced drop [5,9]. Wang [9] derived a simple relation for the coalescence-induced velocity of two droplets based on the energy conservation of surface energy, viscous

dissipation energy and dynamic energy. Although their formula can well describe the influence of drop scale on the coalescence-induced velocity, the model does not distinguish micro and nanostructural parameters, thus it cannot show the effect of nano-texture of two-tier structures on the self-propelled motion of a coalesced condensed drop. In addition, Chen et al. [5] tried to explain the mechanism with the jumping of coalesced drop on a Leidenfrost surface. But this surface is hot with high temperature, and drops jump on this smooth surface even without coalescence while condensed drops on cooled smooth surfaces hardly jump. In fact the jumping of a drop on Leidenfrost surface should be caused by rapid vaporization and expansion of the drop on solid-liquid interface. Therefore the jumping mechanism of the two cases is different.

It is of great importance to clarify the jumping mechanism of a coalesced condensed drop on textured surfaces to design suitable super-hydrophobic surfaces and to realize highly efficient dropwise condensation. We thus engaged the following study.

2. Physical model

The process of coalescing of two condensed drops and the later transformation process of the merged droplet until jumping on a super-hydrophobic surface with nano-texture under static condensation environment are shown in Figs. 1 and 2 respectively. The photos above the modeled droplets in the figures are the experimental recordings (see [supplementary material](#)). The entire process is artificially divided into two stages. The first stage shows the coalescing process of two droplets as demonstrated in Fig. 1. During this stage the two centerlines of two droplets continuously close to each other; the contact area of two droplets constantly increases (Fig. 1B–D) until maximum when coinciding (Fig. 1E). This stage is a very complicated process with a very complex droplet

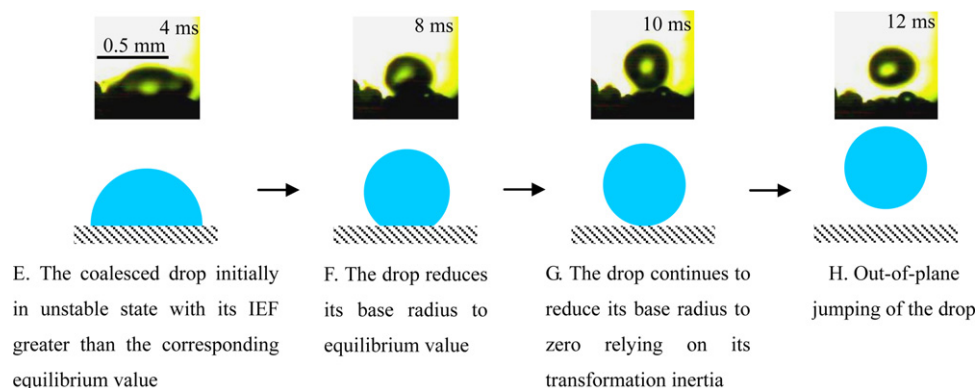


Fig. 2. Coalescence-induced transformation and up moving process of the merged droplet. *Upper photos:* side-view images of self-propelled motion of a merged droplet; *lower:* modeled coalescence-induced drop removal.

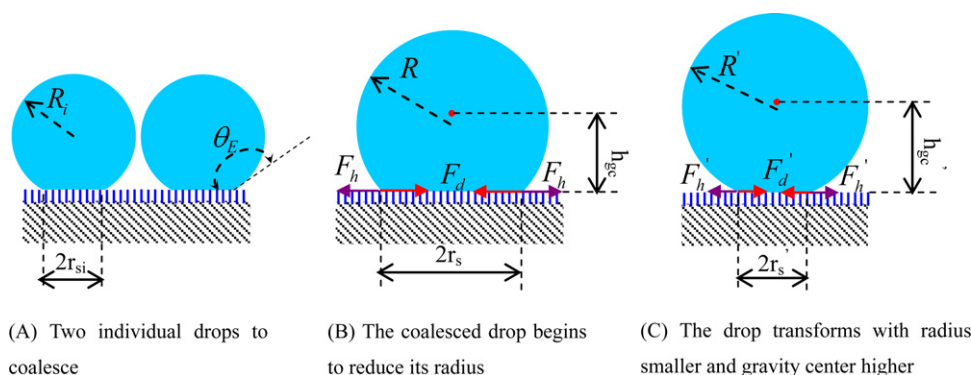


Fig. 3. Schematic for the parameters of droplets before and after coalescence and transformation.

shape during coalescence. The second stage (Fig. 2) illustrates the subsequent process of transformation and jumping of the merged droplet. And we mainly model this stage for a combined drop. It is worth to note that the base area of the merging droplet becomes maximum at the end of the first stage or at the beginning of the second stage, and correspondingly the gravity center of the drop is the lowest. Therefore the time derivatives of these two parameters will be 0 at this time point.

In order to calculate easily while not losing the reliability of mechanism analysis, the shapes of the merged drop in Figs. 1E or 2E, F, and G are approximately regarded as spherical segments. Then the initial state of the merged drop (Fig. 2E) can be determined according to the volume and interface free energy (IFE) before and after coalescence. And the initial IFE of the coalesced drop (Fig. 2E) can be determined by the total IFE of the two drops before merging (Fig. 1A) minus the viscous dissipation energy during the coalescence of droplets (Fig. 1A–E) [9]. For more droplets, the initial state of their coalesced drop can be determined similarly.

The coalesced drop (Fig. 2E) initially is usually in an unstable state with its IFE greater than the corresponding equilibrium value because of the existing of excess IFE [1,5,7,9]. Therefore the droplet will tend to transform itself toward its equilibrium state (Fig. 2F) by reducing its IFE through base radius diminution [1]. The driving force of this transformation process is the difference of surface tension component on surface between unstable and equilibrium states. One of the resistances is the adhesion [10–15] during the base area reduction. The gravity of the drop is another resistance since the drop gravity center will rise up during the transformation process.

When the drop transforms to the equilibrium state (Fig. 2F), it may continue to change its shape to a state with base radius being 0 (Fig. 2G) and even jumping state (Fig. 2H) if its transformation inertia is large enough. We can further divide the process of drop conversion in Fig. 2 into two periods: the first period is from the unstable state to the equilibrium state (Fig. 2E to F), during which the driving force of drop transformation is used to overcome the resistance on three-phase contact line (TPCL) and drop gravity; the second period is further up motion of drop gravity center from equilibrium state (Fig. 2F to G), during which the drop relies on its transformation inertia to continue its shape transition and the resistance includes hysteresis on TPCL, surface tension component away from equilibrium state, and gravity. When the base radius of the drop reduces to 0 and if the up moving speed of drop gravity center is still greater than 0 at this moment, the drop will jump apart from surface with this speed as the initial one.

Since the retardation force on TPCL of a composite drop on textured surfaces is small [12,15], the above drop transformation process can continue until the drop jumps. But for a drop on smooth surfaces or a wetted drop on rough surfaces, it is difficult for the drop to change its shape because of the larger hysteretic force on

TPCL [16]. Therefore, one of the most important conditions for a coalesced drop to jump is the small contact ratio between drop and solid.

3. Mathematical model

3.1. Dynamic equation of drop transformation after coalescence

According to the above physical model and the schematic shown in Fig. 3, the scale of a coalesced drop changes in all directions simultaneously during its transformation from the initial unstable to its equilibrium state (Fig. 2), including the reduction of base radius and increase of gravity center (Fig. 3). The forces acted on the drop in different directions thus coexist and influence each other during the shape transition. For instance, the interfacial tension on TPCL causes the drop to reduce its base radius, and the gravity center rises at the same time while gravity of the drop must be overcome in this process. Therefore, the interfacial tension along solid surface correlates with the perpendicular gravity during the process. In order to comprehensively consider the effect of forces in all directions on the drop deformation, this model correlates these forces with the corresponding energy changes and/or the work done by these forces, so that the dynamic equation to describe the drop transformation can be established according to the energy and work conservation.

The driving force for an unstable drop to change its shape toward equilibrium state results from its IFE decreasing. Therefore, the reduction of the IFE is the same as the work done by this driving force. That is $-dE = F_d(-dr_s)$ can be written, where E is the IFE of the drop, F_d is the driving force to reduce the drop base radius r_s . At the same time, the reduction of this energy equals to the increase of other energy or the work to overcome certain type of resistance according to energy conservation. These include the work done to overcome the retardation force on TPCL $F_h(-dr_s)$, the increase of gravity potential because of the rising of drop gravity center $mgdh_{gc}$, as well as the work done by the drop transformation inertia force $m(d^2h_{gc}/dt^2)dh_{gc}$. Then the energy and work conservation during the drop transformation can be written as:

$$F_d(-dr_s) = F_h(-dr_s) + mgdh_{gc} + m \frac{d^2h_{gc}}{dt^2} dh_{gc} \quad (1)$$

where F_d is the surface tension driving force, F_h is the retardation force on TPCL, m is drop mass, g is gravity acceleration, h_{gc} is the gravity center position of the drop, t is time, r_s is the base radius of drop.

We define $m(d^2h_{gc}/dt^2)$ in Eq. (1) as drop transformation inertia force since the mass of drop focus on the gravity center and the shift of this position represent the motion of the drop during its shape conversion.

After division by $-dr_s$ to each term in Eq. (1), the following equation can be found:

$$F_d - F_h - mg \left(-\frac{dh_{gc}}{dr_s} \right) = m \frac{d^2 h_{gc}}{dt^2} \left(-\frac{dh_{gc}}{dr_s} \right) \quad (2)$$

This is the dynamic equation describing drop transformation in Fig. 2.

3.2. Initial conditions for dynamic equation

The initial conditions for Eq. (2) are $r_s|_{t=0} = r_{s0}$, $h_{gc}|_{t=0} = h_{gc0}$, $(dr_s/dt)|_{t=0} = 0$, $(dh_{gc}/dt)|_{t=0} = 0$, where r_{s0} and h_{gc0} mean their initial values of r_s and h_{gc} .

The initial shape of a coalesced drop (Figs. 1E or 2E) before transformation is defined as such a spherical segment that its volume equals to the sum of all the merging drops and its IFE equals to the total IFE of all the merging drops minus the viscous dissipation energy [9] during the coalescence of these drops (Fig. 1). Taking the merge of two droplets with same size as an example, the initial IFE of the coalesced drop can be expressed as [9]:

$$E_C = E_{\text{drops}} - 72\pi\mu\sqrt{\frac{\sigma_{LG}R_i^3}{\rho}} \quad (3)$$

where E_C is the initial IFE of the coalesced drop, E_{drops} is the total IFE of all individual drops on a surface before merge, μ is the viscosity of liquid, σ_{LG} is surface tension, R_i is the radius of the individual drop, and ρ is the density of liquid. For an individual drop in equilibrium state before coalescence, its IFE is expressed as [9]:

$$E_S = \pi\sigma_{LG}[2R_i^2(1 - \cos\theta_E) - r_{si}^2 \cos\theta_E] + \sigma_{SG}A_{\text{total}} = E_i + \sigma_{SG}A_{\text{total}} \quad (4)$$

where

$$E_i = \pi\sigma_{LG}[2R_i^2(1 - \cos\theta_E) - r_{si}^2 \cos\theta_E] \quad (5)$$

and θ_E is the equilibrium contact angle, r_{si} is the base radius of individual drop, as shown in Fig. 3. And σ_{SG} is the interfacial tension between solid and gas/vapor, A_{total} is the selected total area of the solid surface. Then the total IFE of all droplets, E_{drops} , on the same selected surface area A_{total} is:

$$E_{\text{drops}} = \sum_i E_i + \sigma_{SG}A_{\text{total}} \quad (6)$$

Similarly, the initial IFE of the coalesced drop can be expressed as:

$$E_C = \pi\sigma_{LG}[2R^2(1 - \cos\theta) - r_s^2 \cos\theta_E] + \sigma_{SG}A_{\text{total}} = E + \sigma_{SG}A_{\text{total}} \quad (7)$$

in which

$$E = \pi\sigma_{LG}[2R^2(1 - \cos\theta) - r_s^2 \cos\theta_E] \quad (8)$$

and θ and R are the apparent contact angle and spherical radius of the merged droplet respectively.

After substituting Eqs. (6) and (7) into Eq. (3), we can find:

$$E = \sum_i E_i - 72\pi\mu\sqrt{\frac{\sigma_{LG}R_i^3}{\rho}} \quad (9)$$

Thus the energy E of the coalesced drop can be calculated if the parameters of individual droplets and surfaces are given.

Whence the volume V and the energy E of the coalesced drop are found, its initial base radius and center of mass position can be determined according to Eq. (8) and the relations below [17]:

$$V = \frac{1}{3}\pi R^3(2 - 3\cos\theta + \cos^3\theta) \quad (10)$$

$$r_s = R\sin\theta \quad (11)$$

$$h = R(1 - \cos\theta) \quad (12)$$

$$h_{gc} = \frac{h(4R - h)}{4(3R - h)} \quad (13)$$

in which h is the height of the spherical cap.

3.3. Expressions of the quantities in Eq. (2)

Eq. (2) is not a simple force balance in one direction but covers all driving force and resistances influencing the drop transformation. The surface tension driving force in Eq. (2) equals to the surface tension difference along surface between unstable state and equilibrium state of the drop:

$$F_d = 2\pi r_s \sigma_{LG}(\cos\theta - \cos\theta_E) \quad (14)$$

where θ is the apparent contact angle. θ_E is the same as the intrinsic contact angle θ_0 for a drop on a flat surface, and it can be determined by Young equation. While on a rough surface, the equilibrium contact angle for a Wenzel or a Cassie drop is determined by Wenzel or Cassie–Baxter equation respectively.

Furthermore, for a drop on smooth surfaces, a wetted drop on rough surfaces, a partial wetted drop which only impales micro structure on micro–nano two-tier rough surfaces, and a composite drop on textured surfaces, the hysteretic force of the drop on TPCL for these cases can be expressed as below respectively if adhesion is considered as the cause for the retardation:

$$F_h = 2\pi r_s \sigma_{LG}(1 + \cos\theta_0) \quad \text{on smooth surfaces} \quad (15)$$

$$F_h = 2\pi r_s r \sigma_{LG}(1 + \cos\theta_0) \quad \text{a wetted drop on rough surfaces} \quad (15')$$

$$F_h = 2\pi r_s r_m f_n \sigma_{LG}(1 + \cos\theta_0) \quad \text{a partial wetted drop on two-tier surfaces} \quad (15'')$$

$$F_h = 2\pi r_s f_m f_n \sigma_{LG}(1 + \cos\theta_0) \quad \text{a composite drop on textured surfaces} \quad (15''')$$

where r represents the rough factor in Wenzel equation for a wetted drop on rough surface; r_m means the rough factor of micro structure for a micro–nano two-tier texture surface; f_m and f_n are the Cassie rough factors respectively for the micro and nano rough structures on a hierarchical surface. Besides, $f = f_m \times f_n$ is used in this paper.

It can be found from Eqs. (15)–(15''') that the retardation force is the greatest for a wetted drop on rough surfaces, then is the one on smooth surface. The force may be small for a partial wetted drop on two-tier surfaces depending on the value of $r_m \times f_n$. And obviously the smallest retardation force is the one for a composite drop on textured surfaces.

3.4. Jumping height of a transforming drop

Finally, whether a transforming drop can jump or not depends on whether the up speed of the drop gravity center $(dh_{gc}/dt)|_{r_s=0}$ greater than 0 when its base radius becomes 0. If this speed is

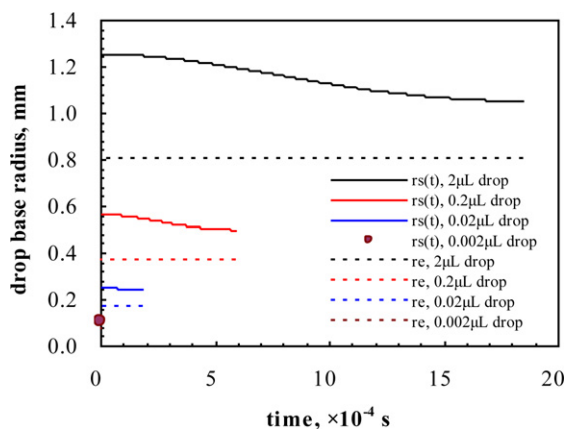


Fig. 4. Transformation curves of coalesced droplets from two same size drops on flat surface with $\theta_E = 110^\circ$. Merged drop base radius changes with time. And the larger a droplet, the longer the time lasts. r_s : drop base radius; r_e : drop base radius at equilibrium state. All the volumes mean those of merged droplets.

greater than 0, the drop will jump with this speed as the initial one. And the out-of-plane height of the drop can be expressed if the friction between drop and air is ignored:

$$H = \frac{1}{2g} \left(\frac{dh_{gc}}{dt} \Big|_{r_s=0} \right)^2 \quad (16)$$

3.5. Solution method for dynamic equation

The three parameters, h_{gc} , θ , and r_s in Eq. (2) change with time. Their relations are shown in Eqs. (8) and (10)–(13). Therefore the changes of base radius and/or gravity center with time can be found with Eq. (2) and its initial conditions being differenced and solved. The calculation will stop if the base radius no longer reduces or if the gravity center no longer rises, which means that the shape of a condensed drop on such surfaces no longer changes. On the other hand, the jumping height can be found according to Eq. (16) if the up speed of gravity center is greater than 0 when its base radius becomes 0.

4. Results and discussions

4.1. No jumping takes place for a coalesced condensed drop on flat surfaces

The transformation curves of coalesced drops with different volumes on a smooth surface are shown in Fig. 4, in which all terminal points on each curve correspond to the time point when drops stop changing their shapes. It can be seen that the merged condensed drops with volumes from 2 nL to 2 μ L can change their shapes only within a limited range after coalescence, namely, their base radii reduce only in certain extent, then stop before reaching the equilibrium radii. Specially for a 2 nL coalesced drop, it will not change its shape after mergence. The retardation force on TPCL is the reason to inhibit the drops further transform toward their equilibrium states. In addition, the calculation results also indicate that the smaller the drop size, the shorter the time lasted in the transformation process. The period can be in milliseconds to one magnitude order smaller for drops from micro liter to nano liter. The smaller the drop size, the smaller its inertia, so that the drop transforms faster, the time needed is thus shorter. But if a merged droplet is too small, such as in 2 nL on a flat surface, the viscous dissipation energy during coalescence may become obvious so that the surplus IFE of the coalesced drop is not large enough to drive the drop transforming.

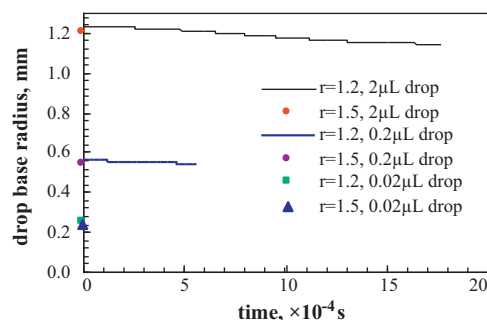


Fig. 5. Transformation curves of coalesced drops from two same size Wenzel drops on rough surfaces. Merged drops on a relatively rougher surface does not transform after coalescence. Only relatively larger drops on a surface with small rough factors can change their shapes after merging. r : Wenzel rough factor. All the volumes mean those of merged droplets.

Since all the drops with these different sizes cannot reduce their radii to 0, these drops on flat surfaces will not jump after coalescence, which is accord with the experimental inspection [5].

4.2. Jumping neither takes place for a coalesced condensed drop in wetted state on rough surfaces

The transformation curves of coalesced drops in wetted state with different volumes on different rough surfaces are shown in Fig. 5. For relatively larger coalesced drops, in 2 μ L or 0.2 μ L, they can reduce their base radii a little on a rough surface with smaller rough factor ($r=1.2$), and stops the shape conversion shortly. But on a rough surface with a little larger rough factor ($r=1.5$), the transformation cannot take place at all after the drops coalesce, as shown with solid dots in the figure, which is caused by the increased resistance on TPCL resulted from the longer TPCL on the surface. If merged drop volume becomes smaller, 0.02 μ L, the drop will not change its shape any more on the surfaces no matter with small or with large rough factors. In general, a coalesced drop from two wetted drops on a rough surface either transforms with limited range or stay there without any shape changing. In fact, the larger the Wenzel rough factor of a surface, the more difficult for a coalesced drop to alter its shape. And a wetted drop on rough surface will be more difficult to jump compared to the case on smooth surface since longer TPCL exists.

It should be mentioned that the above calculated result is very accord with the experimental outcomes for condensed drops on rough surfaces [18–26]. The condensed drops on these micro textured surfaces usually appeared in wetted states, and they hardly move and more impossibly jump.

4.3. Partially wetted drops can conditionally transform to composite state and jump on micro–nano two-tier surfaces

A condensed drop can appear in a partially wetted state on a micro–nano hierarchical surface with the micro structure impaled while nano roughness not wetted [27]. Besides, the early small condensed drops usually stay in the micro textures [1,7] on a two-tier surface, and they will become such partially wetted drops after further combinations [1,23]. We calculated the transformation processes of the partially wetted drops (water and its mixture with ethanol) after coalescence on two-tier surfaces, as shown in Fig. 6. It can be seen that some merged drops can transform into Cassie state by reducing their base radius under certain conditions, which include suitable nanostructural parameters and chemical properties of drops. For the partially wetted water drops on the surface with small Cassie rough factor f_n (0.1), the coalesced drops can convert into Cassie state. But if f_n increases to 0.25 the merged drops

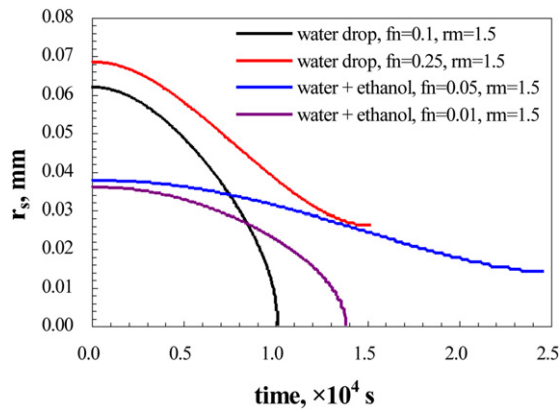


Fig. 6. Transformation processes of coalesced drops from two 1 nL partially wetted drops on two-tier surfaces. Some partially wetting merged droplets can reduce their base radii to 0 under a certain micro–nano structural parameters while the drops may not transform until jump under other structural parameters. r_s : droplet base radius; f_n : the Cassie rough factor for the nano rough structure on a hierarchical surface; r_m : the Wenzel rough factor for the micro rough structure on a hierarchical surface. Water drop: $\rho = 998 \text{ kg/m}^3$, $\sigma_{LG} = 0.072 \text{ N/m}$, $\theta_E = 110^\circ$; water + ethanol: $\rho = 970 \text{ kg/m}^3$, $\sigma_{LG} = 0.04 \text{ N/m}$, $\theta_E = 95^\circ$.

can no longer change to Cassie state. For the partially wetted drops of water/ethanol mixture, they can transform into composite state only under the condition of very small f_n (such as 0.01). If f_n becomes a little larger (0.05), these droplets cannot change to Cassie state. Therefore, the smaller the f_n , the easier for a partially wetted drop to

transform. And the smaller the surface tension and intrinsic contact angle, the more difficult for the drop to shift.

In order to represent the effect of micro–nano two-tier structural parameters in a wide range, the transformation and jumping height of coalesced drops on various textured surfaces were calculated, as shown in Figs. 7 and 8. It is clear from Fig. 7 that water drops can jump in a much wider range of micro–nano structural parameters than the drops of water/ethanol mixture, and the jumping height is also much higher. Fig. 8 clearly shows the micro–nano parameter ranges within which various merged droplets can convert from partial Wenzel state to Cassie state after combination. It can be found that the smaller the f_n , the easier the transformation. When r_m is less than 1.5, the conversion takes place easily, but a successful transformation will need even smaller f_n if r_m is greater than 2.0. Moreover, the transformation of coalesced drops from 3 droplets can take place more easily in a wider range of parameters than the merged drop from 2 droplets. All these results sufficiently reflect the effect of the real length of TPCL of drops on their transformation. The larger the f_n and r_m , the longer the TPCL, then the greater the resistance for the TPCL to move, thus the more difficult the drops to reduce their base radii to transform. On the other hand, the more the drop number to merge, the larger the surplus IFE of coalesced drop, so that the greater the driving force for drop transformation, and the more easily for the drop to change its state.

It is thus clear from the above results that a partially wetted drop can conditionally transform to composite state on a two-tier surface with suitable f_n and r_m parameters. This result is quite similar to the drop state transition Chen et al. reported [27]. They used vibration

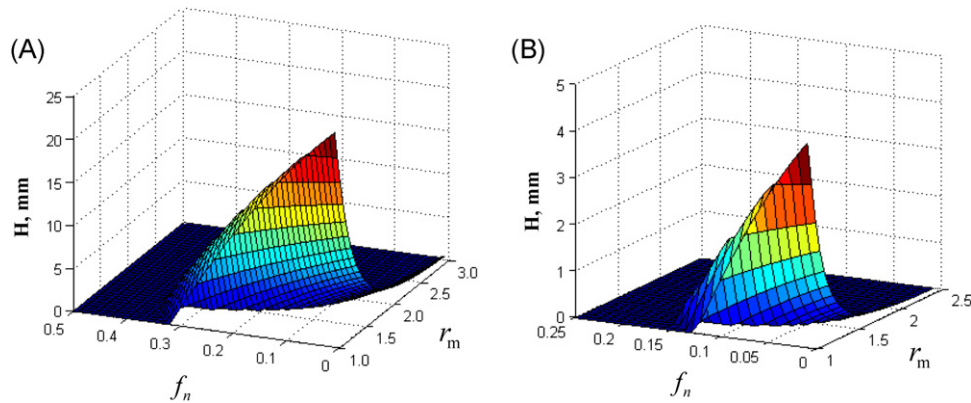


Fig. 7. Coalescence-induced jumping of merged droplets from two 1 nL partially wetted drops on different two-tier surfaces. Some partially wetting merged droplets can jump obviously under a certain micro–nano structural parameters while the drops may not jump or not obviously under other structural parameters. Besides, water droplets (A) jump easier and higher than water + ethanol droplets (B). f_n : Cassie rough factor of nano structure; r_m : Wenzel rough factor of micro structure. (A) water: $\rho = 998 \text{ kg/m}^3$, $\sigma_{LG} = 0.072 \text{ N/m}$, $\theta_E = 110^\circ$; (B) water + ethanol: $\rho = 970 \text{ kg/m}^3$, $\sigma_{LG} = 0.04 \text{ N/m}$, $\theta_E = 95^\circ$.

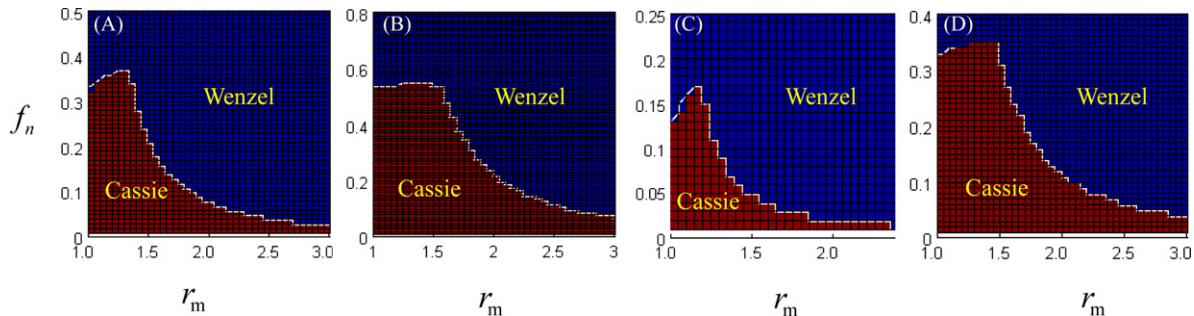


Fig. 8. Coalescence-induced transformation of merged droplets from two (A and C) or three (B and D) 1 nL partially wetted drops on different two-tier surfaces. Coalescence of three droplets can induce the merged drops transform to Cassie state with a wider micro–nano structural parameters than that of two droplets. And water droplets (A and B) transform easier than water + ethanol droplets (C and D). f_n : Cassie rough factor of nano structure; r_m : Wenzel rough factor of micro structure; “Wenzel”: parameter area for droplets unable to transform to Cassie state; “Cassie”: parameter area for droplets able to transform to Cassie state. (A and B): water: $\rho = 998 \text{ kg/m}^3$; $\sigma_{LG} = 0.072 \text{ N/m}$; $\theta_E = 110^\circ$; (C and D): water + ethanol: $\rho = 970 \text{ kg/m}^3$; $\sigma_{LG} = 0.04 \text{ N/m}$; $\theta_E = 95^\circ$.

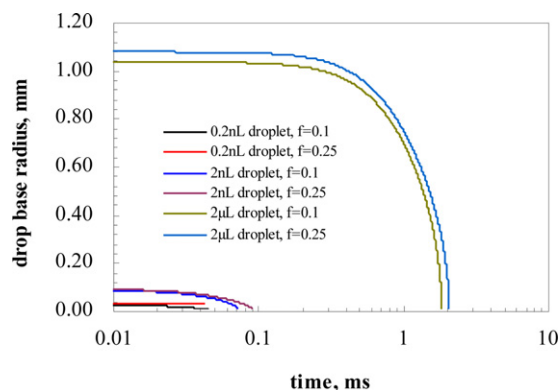


Fig. 9. Transformation curves of coalesced composite drops from two same size Cassie drops on nano or micro–nano two-tier surfaces. Coalesced droplets with wide volume range from nano liter to micro liter all can reduce their base radius to 0. But when the drop volume decreases to 0.2 nL, the merged drop will not transform until jumping if Cassie rough factor f is not small enough (0.25). All the volumes mean those of merged droplets.

energy to make the partially wetted drops on the two-tier surface transit to Cassie state. While our result demonstrates that the driving force from surplus IFE after the coalescence of two condensed drops can also make such partially wetted drops change their shape to composite state. The only difference of the two processes is the distinct driving force.

4.4. Composite drops after coalescence easily jump on rough surfaces with nanostructure

Different from the partially wetted drops on two-tier surfaces, a coalesced drop from two Cassie state drops will transform and jump much more easily because it has shorter TPCL. Fig. 9 shows the calculated transformation curves of coalesced composite drops with different volume on rough surfaces with different Cassie rough factors. It can be seen that the coalesced condensed drops with wide volume range from nano liter to micro liter all can reduce their base radius to 0. But when the merged drop volume decreases to 0.2 nL, the drop will not transform until jumping if nano parameter f_n is not small enough (0.25). This means the scale of a coalesced drop affects its transformation and jumping significantly.

In order to sufficiently represent the effect of drop scale on its bouncing, the jumping heights of merged drops with different sizes were calculated based on the up speed of their gravity centers when the base radiuses become 0, and the results are shown in Fig. 10. It is thus clear that both too small and too large drops cannot jump. On the one hand, the gravity will dominate the behavior of a large drop. In fact, the scale of a larger drop may approach to capillary length. For example, the diameter of a 1 μ L drop on hydrophobic surface is 1–2 mm, while the capillary length is about 2 mm [28,29]. Therefore, gravity of larger drops will govern their transformation and larger drops are difficult to jump after coalescence when their size comes close to capillary length. On the other hand, when the scale of a drop decreases to a few tens micrometers, the viscous dissipation energy during merge will become dominant since this dissipation energy declines with the size decrease of drops slower than IFE of drops. Therefore, the merged drops smaller than a few tens of micrometers will not jump. This is consistency with the experimental inspections by Chen et al. [5]. They observed that the condensed drops on two-tier surfaces could jump only after their size became greater than 10 μ m.

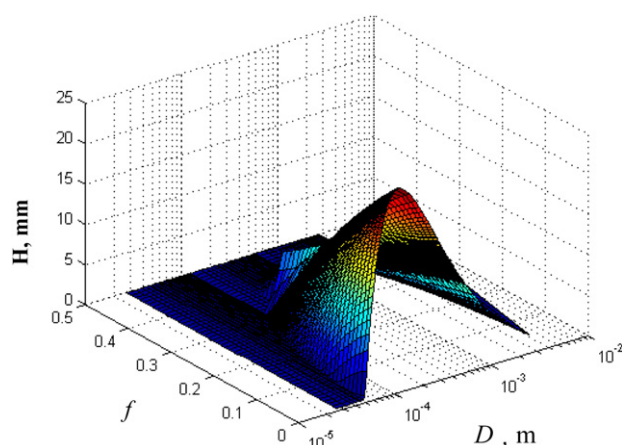


Fig. 10. Coalescence-induced jumping of merged droplets from two same size Cassie drops on textured surfaces. Both too small and too large drops cannot jump. H : drop jumping height; $f = f_m \times f_n$, f_m and f_n are the Cassie rough factors respectively for the micro and nano rough structures on a hierarchical surface; D : diameter of coalesced drops. All the droplets considered here are larger than microscale roughness scale.

4.5. Coalescence-induced jumping of two drops with different scales

All above results are limited to the coalescence-induced jumping of droplets merged from two same size drops. However, the drop scale distributes quite unevenly on a dropwise condensation surface. Often it is the two or more drops with different sizes that merge. Fig. 11 shows the calculated result for the coalescence-induced jumping height of merged droplets from two drops with different scales. It can be found from Fig. 11A that the size of smaller drop must exceed 60% of larger drop to make the coalescence-induced jumping take place when the larger drop is 1 nL (124 μ m in diameter), otherwise the insufficient surplus IFE cannot drive the merged drop to jump if the smaller drop is too small. While the larger drop becomes 1 μ L (1.1 mm in diameter), the coalescence-induced jumping becomes easier. In this case the size of smaller drop only needs over 40% of the larger drop.

4.6. Coalescence-induced jumping for a larger drop to absorb a number of smaller satellite drops

Dropwise condensation on micro–nano textured surfaces is a typical process of larger droplets continuously absorbing their peripheral small satellite drops [30]. And condensed drops grow up mainly in this way until moving away from surfaces. Therefore, it is necessary to investigate the coalescence-induced transformation and motion after a larger drop absorbs smaller droplets of different scale and different number. Fig. 12 shows the coalescence-induced self-propelled motion of a larger drop (124 μ m) swallowing up a number of smaller droplets (26.4 μ m) (A) and (9.8 μ m) (B). It can be seen that the coalescence-induced self-propelled motion can take place when 5–6 26.4 μ m smaller drops are absorbed. But if the smaller drops are under 10 μ m, too many satellite drops are needed to absorb simultaneously for the larger drop to jump. In fact, this situation is hardly happening, the drop is almost impossible to jump. It can be concluded that a larger drop has to combine with other not too small drops to move away from the surface.

4.7. Further discussions

The difference between this model and the one of Wang et al. [9] should be pointed out. Wang's model was based on the conservation of a few types of energy. However, energy is a kind of

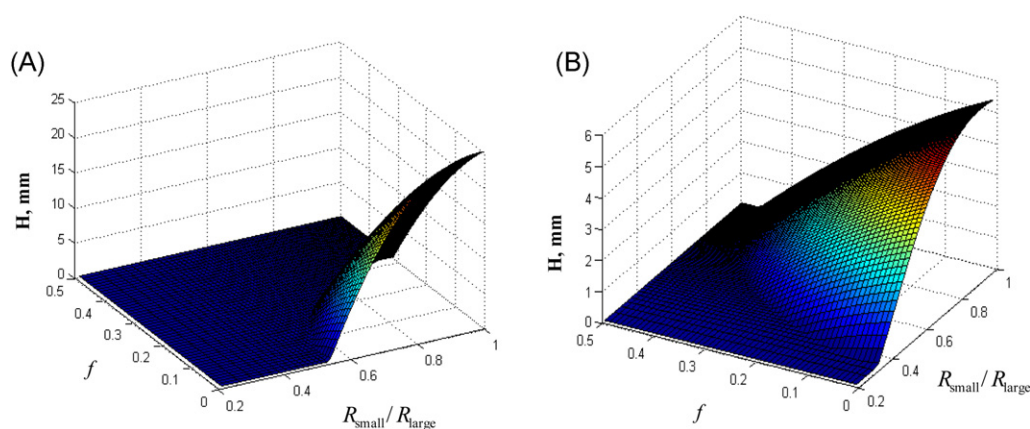


Fig. 11. Coalescence-induced jumping of a larger Cassie drop merged with another smaller Cassie drop. (A) and (B) represent 1 nL and 1 μ L larger drops respectively. H : drop jumping height; $f = f_m \times f_n$, f_m and f_n are the Cassie rough factors respectively for the micro and nano rough structures on a hierarchical surface; $R_{\text{small}}/R_{\text{large}}$: radius ratio of small drop and larger drop.

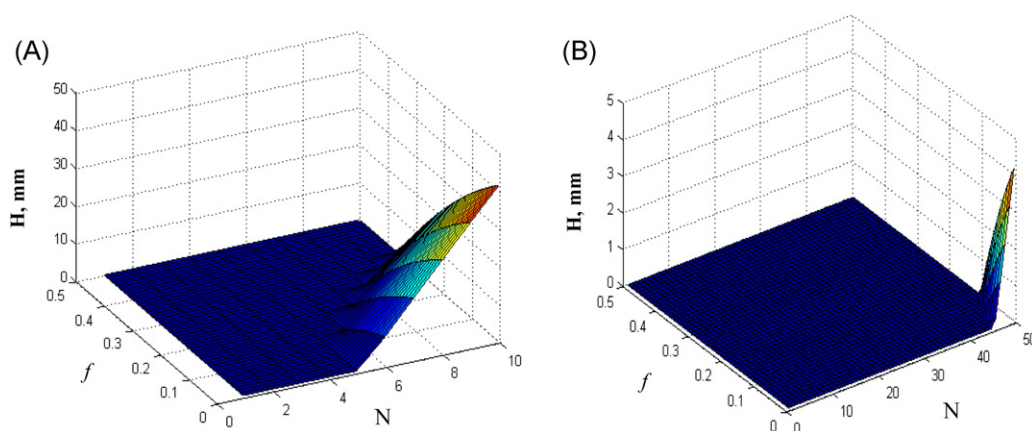


Fig. 12. Coalescence-induced jumping of a 1 nL Cassie drop (124 μ m in diameter) absorbing a number of small satellite droplets. (A) and (B) represent satellite drops with diameter of 26.4 and 9.8 μ m respectively. The coalescence-induced self-propelled motion can take place when 5–6 26.4 μ m smaller droplets are absorbed. But if the smaller drops are under 10 μ m, too many satellite droplets are needed to absorb simultaneously for the larger drop to jump. H : drop jumping height; $f = f_m \times f_n$, f_m and f_n are the Cassie rough factors respectively for the micro and nano rough structures on a hierarchical surface; N : the number of satellite droplets absorbed.

state function, only with which it is difficult to determine if a dynamic process can proceed or not since the resistance of the process or energy barrier is unknown. Also a continuous time-dependent process cannot be illustrated only with the energy conservation of a few separated states. Besides, their model could not demonstrate the effect of nano-texture of two-tier structures on the self-propelled motion of a coalesced condensed drop. In our model we not only considered IFE, but also the process work done by some forces, such as the work done to overcome the retardation force on TPCL. Moreover, our Eqs. (1) and (2) are differential equations and can represent the continuous time-dependent process of a coalescence-induced droplet transformation. Besides, our model also considered the effect of both micro and nanostructural parameters on the self-propelled jumping of a merged drop.

A similar research about droplets deformation should also be mentioned. Wang et al. [31] studied the rebounding of a head-on drop when it collided another droplet below with a certain speed. This kind of rebounding is caused by the elasticity of two droplets when they deform their shapes. And it needs a certain collision speed or short contact time for the two droplets. Moreover, such rebounding without droplets coalescence is different from the coalescence-induced jumping of condensed drops. There is no clear elasticity shown when nearly static condensed droplets coalesce and they simply merge. Also the reported rebounding can take place on a flat surface while jumping of condensed drops happens only on

a super-hydrophobic surface with nanostructures. Therefore, the mechanism of the two phenomena should be different.

Finally, there are still some limitations of the present model. For instance, the momentum during coalescence was not considered, that may influence the later jumping process; the drops moving before merging was also not included, which typically exists in the condition of continuous dropwise condensation. Although this model can explain the main mechanism of condensed drops jumping on super-hydrophobic surfaces, further improvement is needed to make the model closer to the real dropwise condensation process.

5. Conclusions

The jumping mechanism of a condensed drop on super-hydrophobic surfaces is that the initially coalesced drop is in unstable state so that it has the driving force to reduce its base radius toward its equilibrium state. Also the nanostructure is the other key point for a condensed drop to appear in composite state and to reduce the retardation force during the transformation of a coalesced drop. If the gravity center up speed of the drop is greater than 0 when its base radius becomes 0, the self-propelled out-of-plane motion of the condensed drop will take place.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2012.08.063>.

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